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Solid oxide cell R&D at Risø National Laboratory—and its transfer to technology

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Abstract Risø National Laboratory has conducted R&D on solid oxide cells for almost 20 years—all the time together with industries with interest in deploying the technology when mature. Risø National Laboratory (Risø) and Topsoe Fuel Cell A/S (TOFC) have for several years jointly carried out a development programme focusing on low cost manufacturing of flat planar anode-supported cells and stacks employing metallic interconnects. The consortium of Risø and TOFC has up-scaled its production capacity of anode-supported cells to about 1,100 per week. New generations of SOFCs are being developed by the consortium, e.g. a metal-supported cell. TOFC has an extended program to develop the SOFC technology all the way to a marketable product.

Keywords Fuel cell · Solid oxide fuel cell · SOFC · Anode-supported · Metal-supported · Interconnect · Coatings · Pilot factory

1 Introduction

At Risø National Laboratory the R&D on SOFC began in 1989. A survey conducted by Risø National Laboratory together with Haldor Topsoe A/S, Innovosion A/S, Danish utilities, universities and the Danish Energy Agency led to the conclusion that fuel cells might be important in the future energy supply, and that the opportunities for the Danish players (industries, universities, research centres, utilities) probably would be best in the area of SOFC of the different types of fuel cells. The prospects for this technology was foreseen to be very positive.

The first projects at Risø were focused on the manufacture of tape casted yttria-doped zirconia (YSZ) electrolytes. The electrolyte was about 200 μm thick. Conventional Ni/YSZ cermets and YSZ/LSM (Lanthanum–strontium–manganites) composite electrodes were developed and deposited by wet spraying. These materials were well-known from the literature (for an overview, see e.g. [1]) and were used by several developers around the world. The flat-plate cells were tested in hydrogen/air at about 1000°C. The design of choice was already at that time the flat-plate design, especially due to the high power density possible. High operating temperatures (around 1000 °C) were needed to keep the area-specific resistance (ASR) of the electrolyte-supported cells at an acceptable level, the sizable activation energy of the electrolyte being responsible for a rapid increase in resistance at lower temperatures.

Due to the high operating temperatures the interconnects were based on ceramics. The requirements to the interconnector, at all operating temperatures, are stringent and include having good electronic conductivity, low ionic conducitvity, gas tightness, good thermal conductivity, high mechanical strength, thermal expansion coefficient compatible with the cell, and good corrosion resistance. A ceramic lanthanum-strontium-chromite perovskite material was developed as an interconnect material. In 1995 a 500 W stack consisting of 70 cells (of which 20 later were by-passed) was erected and operated [2]. The stack proved the technology, but did also point to a number of issues to be solved. Also, economical analyses performed by Haldor Topsøe A/S and Risø National Laboratory pointed out that in order to make the SOFC flat-plate technology commercially available, the cost of the materials of the stack had to

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be reduced. The cost of the rather thick (about 2 mm) machine profiled ceramic interconnector was anticipated to be too high. This pointed to the use of a metallic interconnector. In order to be able to fulfill especially the corrosion requirements, the operating temperature had to be reduced. It was decided to aim for an operating temperature of about 850 °C. A chromium-rich alloy was chosen, namely the $Cr_{95}Fe_5$ alloy with Y_2O_3 particles added, developed by Plansee [3]. The lowering of the operating temperature could only be accepted if the performance of the cells would be much improved at this lower temperatures. This required the development of a new type of cell, the anode-supported cell, with a thin 10–30 μm thick YSZ electrolyte and much improved electrodes for the operation at lower temperatures. This was obtained by still using the conventional materials: YSZ, LSM and Ni now with improved microstructures, grading and modified compositions. Such an anode-supported cell was developed at Risø National Laboratory in 1998. A small stack with an anode-supported thin-electrolyte cell and a metallic interconnector with proper coatings and gas distribution and current collection layers was tested successfully in 2000 [4]. This result together with other progresses in the R&D convinced Haldor Topsøe that there was a possible successful route to a commercial SOFC product. This led to the formation of a consortium between Risø National Laboratory and Haldor Topsøe A/S with the goal to develop the solid oxide fuel cell (SOFC) technology into a commercial product. The consortium agreement between Risø National Laboratory and Topsoe Fuel Cell A/S (a spin out from Haldor Topsoe A/S) was renewed in 2006 for another 5 year period.

2 Mission and strategy

The mission of Risø National Laboratory and Topsoe Fuel Cell A/S in their consortium is to make their SOFC technology commercial on the global market. Risø's role is to perform high-quality R&D for the best and competitive progress on the development of cells and other stack components. This covers many aspects of R&D, including e.g. ceramic processing, mechanical properties, electrochemical testing, modelling, chemical engineering, microscopy and other structural characterisation techniques, primarily focusing on the cell and component development. The role of Topsoe Fuel Cell A/S (TOFC) is to develop the stack technology, to industrialise the cell and stack production for the different applications. The system development takes place in cooperation with industrial partners in the different market segments. Risø National Laboratory and Topsoe Fuel Cell A/S is up-scaling the production in a pre-pilot manufacture facility, and the technology and know-how is then to be transferred to a TOFC factory. At Risø improved cells and components, and the next generation of cells and stacks are continuously being developed.

3 R&D activities at Risø

The SOFC activities at Risø involve today about 70 persons or 50 man-year per year. The SOFC type developed is still the flat-plate design. The present R&D is focused on anode-supported and metal-supported types of cells. The standard cell sizes are today 12×12 and 18×18 cm^2 with a total thickness of about 350 μm and with a thin, about 10 μm, zirconia-based electrolyte. The different types of fuel cell designs are sketched in Fig. 1. Thin-film cells for operation at lower temperatures (towards 400 °C) are also being investigated at Risø National Laboratory. Such low temperature SOFC are also being developed internationally [5].

Several standard ceramic forming methods are being used to manufacture the cells and the other stack components. The ceramic processing methods used imply high degrees of shrinkage during the sintering procedures, and it is challenging to obtain cells with the proper dimensions and specific properties. Ceramic processing skills are hence an integral part of the development of high performance and durable cells at Risø National Laboratory. A pre-pilot plant for the manufacture and the development of cells has been built at Risø. The purpose of the pre-pilot plant is to up-scale the processes from the laboratories, and to demonstrate that many cells can be made within the required specifications. The pre-pilot feeds today the cell and stack testing at Risø, at TOFC and at partners around the globe. Figure 2 shows the number of cells produced in the pre-pilot plant. In 2007 14,000 cells were produced.

The pilot plant production facility for the manufacture of anode-supported (2G) cells has recently been upgraded with an automated continuous spraying process, improved screen printing facilities and extra sintering capacity resulting in a weekly production capacity exceeding 1,100 12×12 cm^2 cells. The composition of the 2G cell has been frozen since 2004 and focus has been on improvement of the manufacturing process aiming at improved performance

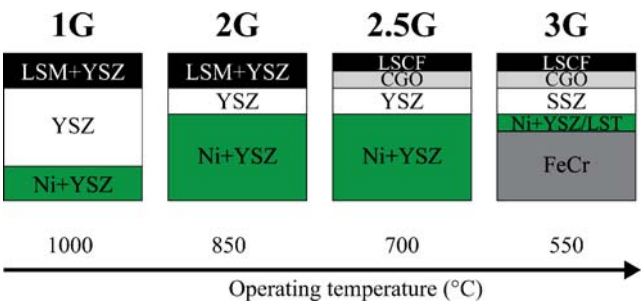

Fig. 1 Various cell generations being developed and produced in the TOFC/Risø consortium

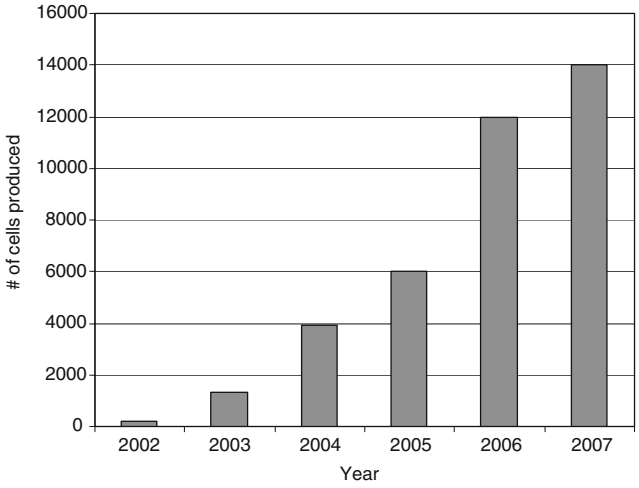

Fig. 2 Number of anode supported 12×12 cm^2 cells produced per year from 2002 to 2007

as well as reduction of rejection rate. The cell size has been scaled up such that cells in the size of 18×18 cm^2 are routinely produced. The largest cell manufactured so far is 1,250 cm^2.

A completely new cell type based on an Fe-Cr alloy support for operation below 700 °C is also being developed. For this cell type it is not only the support material that is new; cathode, electrolyte and anode are also based on a new materials choice. So far, 3G cells up to 12×12 cm^2 have been manufactured successfully. However, the electrical performance still lacks behind that of the anode supported cell.

Wet spraying has been used for many years to deposit micrometer-thick films of electrode or electrolyte materials. One of the challenges using this method is to control the thickness over the whole cell area, and the waste and environmental impact are issues of concern. Screen printing is a well-known process, where waste and thickness control is quite well established. These and other thick/thin-film techniques are used for the making of cells. In general, the introduction of a new process necessitates an intensive development program to adjust slurry, paste and properties optimally.

For several years the electrolyte of choice has been 8 mol% yttria-stabilized zirconia, YSZ. This compound has a number of attractive properties, most notably a sizable ionic conductivity in combination with chemical and mechanical stability at elevated temperatures. In electrolyte supported cells the major part of the internal losses in the cell is associated with the YSZ electrolyte. This is no longer true for an anode supported cell operated at, e.g., 750 °C. However, when the operation temperature is lowered further the electrolyte resistance again becomes dominant. This motivates the search for new electrolyte materials for intermediate temperature SOFCs, such as the metal supported cells. Scandia doped YSZ (ScYSZ) can exhibit a higher ionic conductivity than YSZ [6], and a conductivity that can be maintained without severe degradation over time. For these reasons ScYSZ is being pursued as a possible electrolyte material. The durability, the effect of impurities/doping [7] and the mechanical properties are being investigated at Risø and by partners. Figure 3 shows the conductivity of various electrolyte materials versus inverse temperature.

The anode in most SOFCs world-wide is a Ni-YSZ cermet. Ni is the electrochemically active material, while the YSZ acts as a backbone, keeping the Ni-particles from agglomerating and giving good adherence to the YSZ electrolyte. It is usually made by mixing NiO and YSZ particles. Upon initial reduction, the NiO particles are reduced to metallic Ni, shrinking in the process, and thus creating the porous Ni-YSZ structure. The major problem with the Ni-YSZ anode concerns redox stability: Upon re-oxidation the Ni particles grow, creating internal stresses which ultimately tends to break the cell. Even if the stresses are contained, the growth and subsequent agglomeration of the Ni particles under re-reduction reduces the activity of the anode. The microstructure of the Ni/YSZ anode dependence on the history and treatment is an important subject. The control of the microstructure such that e.g. the expansion upon re-oxidation is minimized is also investigated at Risø [9].

Efforts are made in trying to develop a metal-free anode, since this could increase redox stability markedly. Risø National Laboratory has recently had some success in this direction. Among the materials investigated are doped

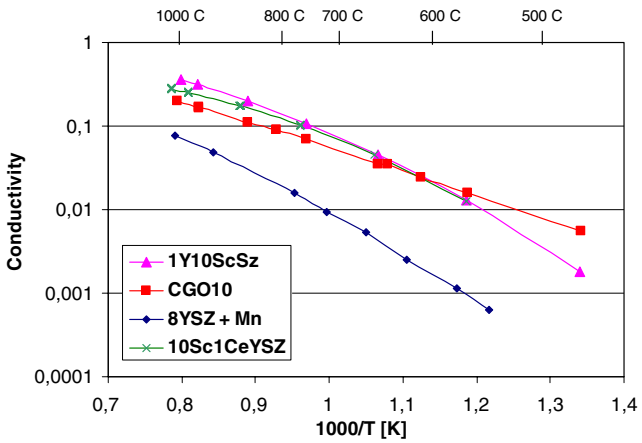

Fig. 3 The total conductivity as a function of the inverse temperature. (8YSZ + Mn resembles an 2000 h aged YSZ) [8] (D. Lybye, unpublished data). The triangles and the crosses show the result of some newly developed zirconia based materials doped with Y, Sc and Ce. CGO10 is 10 mol% gadolinia doped ceria, which is a common electrolyte material at low temperatures. Above approximately 500 °C the total conductivity is a mixture of ionic and electronic conductivity. For the other compositions in the figure the ionic transfer number is very close to one

titanates [10]. The performance under various conditions is under investigation.

The cathode material is still often strontium-doped lanthanum manganite (LSM), mixed with YSZ to increase the triple phase boundary and to ensure good adherence to the electrolyte. Since the cathode accounts for the major part of the internal losses in high-performance cells, many new materials have been investigated. Lanthanum-strontium-cobaltite (LSCo) and lanthanum-strontium-cobaltite-ferrite (LSCF) are promising candidates [11]. They have demonstrated performances that allow the cell temperature to be lowered towards 600°C. However, LSCF tends to react detrimentally with zirconia-based electrolytes due to transport of Sr from the cathode to the YSZ. A doped ceria buffer layer between the cathode and the YSZ electrolyte can minimize unwanted reactions. Such layered cells are being manufactured at Risø in several projects with improved performance. Degradation is, however, still an issue.

The pre-pilot production relies on a spraying process for cathode deposition. Due to the ease of up-scalability and with the aim to further improve the reproducibility of the cell production. From 2003 to 2005 the average area-specific resistance at 850°C was reduced from 0.24±0.05 to 0.15±0.01 $\Omega \cdot cm^2$. Screen printing is being investigated as an alternative route. Cathode performances measured on screen printed cathodes (symmetrical cells based on 150 μm zirconia tapes) are compared to sprayed ones in Fig. 4 (M. Wandel, manuscript in preparation). Evidently, the screen printed cathodes match the sprayed cathodes, and this process is thus considered for use on future large area cells.

Ferritic steel (Fe-Cr alloys) have been identified as good candidates for cheap metallic alloys which can fulfill the requirements listed in the Introduction. A composition around $Fe_{78}Cr_{22}$ has been suggested to be a good choice with respect to especially the corrosion and thermal expansion properties [12]. Such alloys are now being developed by several steel companies. Risø has in particular worked with Sandvik on this development, together with Topsoe Fuel Cell [13]. Good alloys are now available from different sources. Coatings of the steels are to be preferred in order to ensure good electrical contact and in order to achieve the best oxide scale on the alloy, and in order to reduce the effect of Cr-evaporation from the alloy to active cathode sites [14]. New coatings, coating techniques and tests of the performance are important tasks at Risø. Recently, the degradation rate of a TOFC stack has been reduced to below 0.5% per 1,000 h by introduction of improved stack component materials including improved metallic interconnects and improved ceramic coatings [15]. These coatings have proved to protect the cathodes from chromia poisoning at the same time as a low area specific contact resistance of the protected steel of 2–3 $m\Omega cm^2$ is obtained.

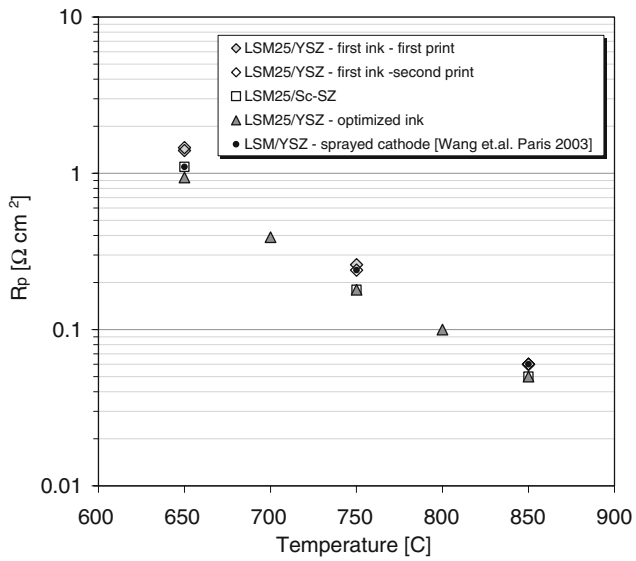

Fig. 4 Polarization resistance of symmetric cells with YSZ/LSM cathodes on YSZ electrolyte (M. Wandel, manuscript in preparation)

The SOFC program comprises development of next generation cells with metallic support for operation at lower temperature in the range 600–750°C. As shown in Fig. 1 the material choice for this cell type differs from previous cell generations in that porous ferritic steel is used as a ductile, robust cell support and the electrolyte is based on scandia doped zirconia with increased durability, lower cost, and high mechanical robustness. Furthermore, the metal supported cells offer a significantly improved tolerance towards redox cycling and improved temperature distribution during cell and stack operation. The next generation stack design under development is based on these cost effective metal supported cells. The stack concept includes a further efficient integration of the individual stack components and more reliable seals leading to lower weight, lower cost and maximal robustness. For metal supports, Fe–Cr steels are materials candidates. Corrosion aspects will probably dictate the operating stack temperature to be below, say 650 °C. If the metal is supporting the cell on the anode side, corrosion may be less of an issue than if supporting the cathode side. In any case, corrosion is probably of most concern with respect to the long term stability of the cell. These issues are under investigation.

Electrochemical cell testing is naturally an important subject in the development of solid oxide cells. In the cell test stands the cells are exposed to various conditions such as different operation temperatures, different fuels, fuel "impurities" (e.g. sulphur), different current loads and voltage drops, short and long time tests (see e.g. [16]). These electrochemical tests, together with a number of other advanced characterization methods, e.g. microscopy,

are essential for the development of improved cells in the pre-pilot plant.

The 2G cells manufactured in the production line are generally very durable at high temperature (850°C) even at very high current loads [16]. The degradation rate increases with increasing polarization. At a current density of 0.25 A cm^{-2} (operating voltage ~850 mV) the voltage degradation rate may be less than 0.25%/1,000 h and at 1 A cm^{-2} (corresponding to an operating voltage ~750 mV) the degradation is below 0.6%/1,000 h. Operating the cells at 750 °C also provide excellent durability when operating at normal polarisation levels. However, under severe operating conditions at 750 °C, i.e. exposed to a strong polarization, a marked degradation is observed [16]. This degradation has been identified to mainly originate from the cathode/electrolyte interface. Efforts are being devoted to develop cells that are also capable of long term operation under these conditions, to enhance the window of operation of the technology. Recently, progress has been achieved in this field [17].

When using fuel derived from biomass in SOFCs, one must be aware of trace amounts of different impurities which may act as poison for the electrochemical processes. One such impurity is H_2S, which is also used as odorant in natural gas lines. The sulphur tolerance of the anodes is currently studied. The effect of small amounts of H_2S in hydrogen on the performance and durability of a "standard" 2G cell was studied at 850 °C and 1 A cm^{-2} (see Fig. 5). The cell voltage decreased and the degradation rate increased during the periods under H_2S. However, these changes were completely reversible up to the studied concentration of 100 ppm H_2S. Turning off the sulphur addition results in a recovery of the cell performance over a period of ~250 h, and the overall degradation tracked over 2,000 h is less than for the reference case. Thus, it is concluded that the sulphur reduces the reaction rate by passivation of reaction sites by adsorption.

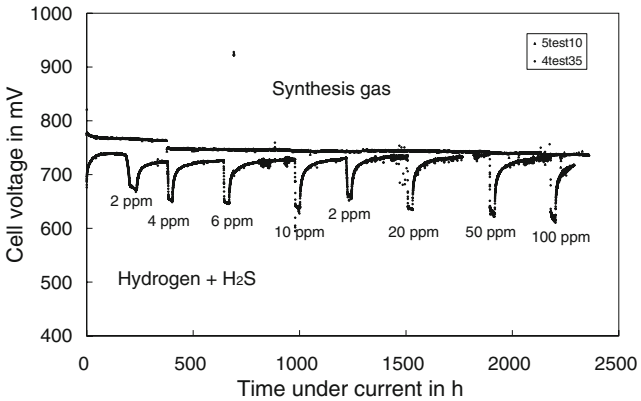

Fig. 5 Cell durability at 850 °C, 1 A cm^{-2}. The upper curve is for a cell operated in syn-gas with a fuel utilization of 75%. The lower curve is for a cell operating at the same temperature and current load but in hydrogen with various amounts of H_2S added periodically (J. Rasmussen et al., manuscript in preparation)

While SOFC fabrication methods have seen dramatic improvement leading to better cell performance, the developments of materials and fundamental concepts have been more incremental. To a large extent this is due to the still incomplete understanding of the cell processes at the most fundamental level. The cell nanostructure plays a crucial role and even minute quantities of impurities may affect the performance dramatically. These facts indicate the need for an increased focus on the fundamental materials issues involved. For this reason Risø has initiated a new Strategic Center for Electrochemistry (SERC). Here fundamental issues, but with a clear interplay with the applications, of solid oxide cells will be treated. Other fundamental projects, primarily conducted by PhD's, have also previously been initiated.

Advanced microscopical methods are believed to be routes to assist the development of improved solid oxide cells. At Risø a controlled-atmosphere high temperature scanning probe microscope (CAHT-SPM) is being developed together with an industrial partner. The goal is to develop this technique for the study of interphases, such as electrolyte/electrode interphases at the typical operating temperatures, and that both microscopical studies and electrochemical studies on a μm-scale can be conducted to gain new knowledge.

Such investigations are motivated by the fact that the performance of high-performing electrodes, which often consist of two interpenetrating phases forming a porous network, depends on the interplay of a large number of factors, including the properties of the constituent phases, their volume ratio, the porosity and percolation of the network, the electrode-electrolyte adherence, and the level of impurities present. In-situ microscopical methods such as the CAHT-SPM may help in achieving a better understanding of the effect of impurities and for developing ways of mitigating their impact.

4 Transfer of R&D to industry

SOFC development has reached a level of maturity which makes it relevant to engage in demonstrations on a wider scale. Both nationally and at the EU level the funding for SOFC demonstrations are set to increase markedly in the coming years. This makes a timely transfer of knowledge from research institutions to industry ever more important.

An important aspect of the transfer of the Risø R&D to technology is the education, at Risø, of technicians and engineers from the industry. This is primarily conducted at the cell manufacture pilot plant at Risø National Laboratory, which comprises equipment for large-scale slurry preparation,

continuous tape casting, screen printing and spray deposition facilities. One aim of the pilot plant is to develop and demonstrate the up-scaling of reproducible, highly-performing SOFCs for use in the development of improved cells and stacks, and for the demonstration of the SOFC technology. Topsoe Fuel Cell is building a pilot-factory for the manufacture of up to 200,000 cells and 2.000 stacks a year. This facility is due to open in 2008.

Two Danish demonstration projects funded by Energinet.dk, the operator of the Danish gas and electricity transmission grids, have been initiated. One is aiming at demonstrating a 1 kW_e micro-CHP (combined heat and power) unit for deployment in private households; this so-called Cluster Project is led by Danfoss A/S with the participation of Topsoe Fuel Cell and others. The other project is a 10 kW_e stack demonstration facility including fuel processing and power conversion located at a power station in Copenhagen, Denmark.

The Finnish engine company Wärtsilä has in 2006 operated a 4 kW prototype with stacks from Topsoe Fuel Cell, fed on pre-reformed, desulphurized Russian natural gas and connected to the grid. In 2007, a 20 kW prototype from Wärtsilä and Topsoe Fuel Cell was operated, as a stepping stone to a 125–250 kW system for marine power and decentralized landbased systems operated on e.g. bio-methanol.

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